

Measurements of ClO and CO₂ for ACCENT

Final Report for NAG 2-1306, covering the period March 1, 1999 to February 29, 2000

Darin Toohey
Program in Atmospheric and Oceanic Sciences
Campus Box 311, University of Colorado
Boulder, 80309-0311

Objectives

Observations have shown that ozone is largely removed in rocket plumes within an hour of launch [M.N. Ross, et al., *Nature* 390, 62-64, 1997]. Large abundances of chlorine oxide (ClO) were first detected in the fresh plume of a Delta rocket in May of 1998 from the NASA WB-57 during the Air Force RISO campaign by the CORE instrument developed at UC Irvine. Similar abundances were detected a month later in the plume of an ATLAS II rocket. Although the maximum ClO observed in these plumes was twenty-five times larger than the highest values ever observed in the perturbed polar vortices, in a new study, [M.N. Ross, et al., *Geophys. Res. Lett.*, 2000, in press] *could not account for observed ozone losses based on known chlorine photochemistry.*

New measurements were obtained in plumes of Delta, Atlas, and Athena rockets in 1999 during ACCENT with the CORE instrument augmented with a modified LiCor non-dispersed infrared detector for fast-response measurements of carbon-dioxide (CO₂). The absolute abundance of this specie constrains the rocket emission stoichiometry, and its relative abundance serves as a tracer of dilution. *The combination of ClO and CO₂ will provide important new insights into the temporal and spatial evolution of reactive chlorine partitioning and its dependence on rocket motor type.*

Results I – Instrument Development

The CORE (Chlorine Oxides in Rocket Exhaust) instrument was originally developed at UC Irvine in 1994 to measure BrO *in situ* at part-per-trillion abundances using small, high-altitude balloons to reduce uncertainties in assessments of the impact of methyl bromide on stratospheric ozone. It was modified in 1997 for fast-response, high-precision measurements of ClO (<100 ppt at >1 s⁻¹) in rocket plumes following a request by Dr. Martin Ross of the Aerospace Corp. Chlorine atoms are detected sensitively and selectively by resonance fluorescence at 118.9 nm following reaction with nitric oxide (NO). For observations in narrow plumes, ClO is measured redundantly at three separate distances from the point of continuous injection of NO. The corresponding reaction times of ~5, ~15 and ~25 ms allow for assessment of conversion efficiency necessary to correct the retrieved chlorine atom signals into accurate ClO mixing ratios. Background signals from Rayleigh scatter off nitrogen molecules in ambient air are measured immediately before and after the plume by replacing the flow of NO with an equivalent flow of ultra-zero air (99.9999%).

CO₂ was detected by absorption at 4.3 μm using a repackaged LiCor 6251 non-dispersed infrared analyzer. Flushing times of ~1 s were achieved by compressing the air from

ambient pressure to ~450 mbar using a modified single-stage KNF Neuberger diaphragm pump and maintaining a flow rate of ~500 sccm through the sample cell. Three stages of pressure control using custom-built electronics and MKS 258 proportional valves maintained a constant, near-zero pressure differential between the sample and reference cells of the analyzer limiting short-term CO₂ density variations to less than $3 \times 10^{11} \text{ cm}^{-3}$. The instrument and electronics were packaged in a sealed box, the pressure of which was maintained at the same pressure as the sample cell (~450 hPa) by one of the pressure-control stages.

Size and weight were minimized, and operating costs were significantly reduced, by configuring the instrument for high-precision measurements in plumes, but otherwise ignoring in-flight extensive calibrations for ambient measurements of CO₂ – a procedure that would require the addition of well-characterized standards and precise temperature stabilization. The instrumental drift was typically ~1 ppm or less over the course of a flight and less than 0.1 ppm during the course of plume traverses. Most of the rapid variations were due to attitude changes of the aircraft that are “detected” by the LiCor analyzer because of a gyroscopic effect on the chopper wheel.

The analyzer’s high precision was preserved by oversampling the millivolt output signals at 5 Hz with an Analog Devices synchronous V-F converter referenced to the TTL output of a high-stability 1 MHz Epson crystal oscillator. For a one-second average the response was 0.02 mV/Hz, equivalent to a detection limit of ~0.01 ppm of CO₂, or just below the variability due to pressure fluctuations. The RMS noise of the measurement was typically 8 Hz, or ± 0.05 ppm (1σ) for a one-second average, yielding S/N > 100 for CO₂ > 5 ppm, the typical maximum abundances observed in the rocket plumes. Noise from the first two flights of the instrument in April 1999 using a prototype circuit board was somewhat larger.

Results II – Observations

Measurements were obtained in the plumes of three rocket plumes, April 12, 1999 (Atlas 2AS, Kennedy Space Center), April 15, 1999, Delta II, Vandenberg AFB, and September 24, 1999 (Athena, Vandenberg AFB), and the following milestones were achieved:

1. First science flight of a new CO₂ instrument on the WB-57 aircraft
2. ClO enhancements of > 40 ppb measured initially in plumes of Atlas and Delta, with CO₂ enhancements between 5 and 15 ppm
3. Lower abundances of ClO at lower altitudes, compared to stratosphere, most likely because of competition between $\text{Cl} + \text{RH} \rightarrow \text{HCl} + \text{R}$ and $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$
4. Measurements of CO₂ highly correlated with particle number at 1-3 μm , such that both are excellent tracers of dilution and mixing
5. ClO in plume of Athena rocket than was in plumes Delta II and Atlas rockets

Figures from the September 24, 1999 encounter with the Athena rocket are shown on the following page.

Publications

There are presently no publications from this work, but it is anticipated that several papers will be submitted to peer reviewed journals by year's end.

